Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

CANMET

Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

POTENTIAL APPLICATIONS OF MIXED SOLVENTS IN HYDROMETALLURGY

L.K. Tan
Metallurgical Chemistry Section
Extractive Metallurgy Laboratory

September 1985

Project: MRP-3.0.52.05
Impurities in Copper Refining

MINERALS RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT MRP/MSL 85-120 (LS)

Crown Copyrights Reserved

MICROMEDIA

JAN 21 1986

POTENTIAL APPLICATIONS OF MIXED SOLVENTS IN HYDROMETALLURGY

by

L.K. Tan*

ABSTRACT

Potential applications of mixed aqueous-organic solvents for hydrometallurgical processing have been reviewed with special emphasis on the acetonitrile-copper system. Acetonitrile-$CuSO_4$ refining of crude copper seems capable of yielding a copper product comparable in purity to commercial cathode copper. The chemistry of mixed solvent systems is also discussed, and an experimental program is outlined that would, if implemented, materially advance the understanding of the chemistry of such systems.

---

* Visiting Fellow, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, 555 Booth Street, Ottawa, Ontario K1A 0G1.

APPLICATIONS POTENTIELLES DES SOLVANTS MIXTES EN HYDROMÉTALLURGIE

par

L.K. Tan*

RÉSUMÉ

Les applications potentielles des solvants aqueux-organiques mixtes servant au traitement hydrométallurgique ont été étudiées et une attention particulière a été attachée au système acétonitrile-cuivre. Il semble que l'affinage du cuivre brut par l'acétonitrile-$CuSO_4$ est susceptible de produire un cuivre d'une pureté comparable au cuivre cathodique de qualité commerciale. Ce rapport présente donc un examen de la chimie des systèmes de solvants mixtes ainsi qu'une description d'un programme expérimental qui avancerait réellement la compréhension de la chimie de ces systèmes, s'il était réalisé.

*Scientifique invité, Laboratoires des sciences minérales, CANMET, Énergie, Mines et Ressources Canada, 555, rue Booth, Ottawa (Ontario) K1A 0G1.

INTRODUCTION

The smelting of copper sulphide concentrates leads to the formation of a blister copper which contains >99% Cu together with a number of impurities. To make the copper suitable for most industrial uses, the metal is generally electrorefined in a $CuSO_4$-H_2SO_4 electrolyte. Although this process results in a pure copper product and the recovery of associated by-products, it suffers from long processing cycles and, especially, very high capital costs. There is a general interest in the development of alternate processes which would yield a comparable metal purity, but would overcome some of the difficulties of the electrorefining process.

Chemical refining of either blister copper or copper concentrates with mixed aqueous organic solvents is one potential means of overcoming the problems of conventional electrorefining. Most effort has been focussed on the use of acetonitrile, but various other solvents have also been examined. Some aspects of the chemistry of mixed solvent systems have been reported, but much of the chemistry either is unknown or is largely speculative.

The purpose of this report is to review the available literature on the potential applications of mixed solvent systems in hydrometallurgical processing, and to discuss some of the chemical aspects of such systems. During the preparation of this report, various subjects requiring additional experimental study were identified, and these are outlined as a possible research program which could be conducted at CANMET or by the metallurgical industry.

REVIEW OF THE LITERATURE

ION SOLVATION AND METALLURGY

Protic solvents, such as water, are hydrogen-bond donors; by contrast, dipolar aprotic solvents are not hydrogen-bond donors, but their molecules are highly polar (1). Examples of dipolar aprotic solvents are dimethyl sulphoxide, dimethylformamide, acetonitrile, acetone, etc., all of which are cheap and readily available. By comparison with water, dipolar aprotic solvents offer different acidities and basicities, different redox stabilities, different anion and cation solvating properties, different solvation of uncharged solutes and therefore different rates of reaction (2,3). To obtain a better understanding of these differences, particular emphasis has been placed on the study of activity coefficients of single ions on transfer from water to another solvent (4-7). The influence of solvent effects on the activity is much greater than the effects of increasing ionic strength or temperature in aqueous solution. The activities of ions can be changed by a factor of up to 10^8 in non-aqueous or mixed solvents relative to the corresponding values in water (8). Based on these considerations, solvent effects have been widely used in organic chemistry with the aim of shortening reaction times, increasing yields and minimizing impurities contributed by side reactions. Parker, whose research was in the areas of ion-solvation and organic reaction mechanisms, recognized that water need not be the unique solvent for hydrometallurgical reactions, and he suggested mixed solvents for various hydrometallurgical processes involving copper, silver and gold (9-13).

Acetonitrile and other organic nitriles solvate Ag^+, Cu^+, Au^+, Ru^{2+} and Os^{2+} more strongly than does water; most other cations like Na^+ and particularly the proton are more strongly solvated by water than by

acetonitrile (11). This behaviour is due to Lewis acid - Lewis base interactions[1] coupled with the possible donation of d-electrons to the π^* antibonding orbital of the nitrile group (11). In acetonitrile-water solutions containing sulphuric acid, Cu^+ is much more strongly solvated by acetonitrile than by water, but Cu^{2+} is more strongly solvated by water than by acetonitrile (12). It has also been established that in this medium cupric sulphate is a strong oxidant, comparable to ferric sulphate in water (11,14). As the proportion of acetonitrile in the mixed solvent increases, it is easier to reduce cupric ion to the cuprous state. Cuprous sulphate

$$Cu^{2+} + Cu^{o} \underset{H_2O}{\overset{CH_3CN}{\rightleftharpoons}} 2Cu^{+} \qquad [1]$$

is stable in the presence of >6 moles of acetonitrile per mole of cuprous ion. With less acetonitrile and a greater concentration of water, cuprous sulphate disproportionates to give metallic copper and cupric sulphate (10). Consequently, many reactions which involve Cu^+ ions and do not proceed significantly in water are able to be carried out in acetonitrile-water solutions, and this has important implications in copper hydrometallurgy (14). Generally, leaching reactions do not involve acid dissolution, but occur by redox solvation (12). Leaching is, therefore, rapid. Reaction 1 can be reversed by the distillation of the acetonitrile from cuprous sulphate solutions (thermal disproportionation) by the use of low grade steam.

---

1) Cations (acids) behave as electron acceptors and the solvents (bases) behave as electron donors.

Copper powder is precipitated, leaving water-soluble impurities in the aqueous cupric sulphate solution; both the cupric sulphate solution and the acetonitrile can be recycled to the leaching operation (14-17). Another alternative for obtaining copper from the acetonitrile-water medium is by electrolysis (14-17). A comparison of this process with the conventional cupric sulphate technique is illustrated in equations [2] and [3]. Electrorefining via cuprous ion is a

Anode Cathode

$$Cu \xrightarrow{-2e^-} Cu^{2+} \xrightarrow{+2e^-} Cu \quad \text{(cupric electrode)} \qquad [2]$$

$$Cu \xrightarrow{-e^-} Cu^{+} \xrightarrow{-e^-} Cu \quad \text{(cuprous electrode)} \qquad [3]$$

one-electron process and therefore offers potentially faster refining at a lower power cost than the existing commercial two-electron electrolysis via Cu^{2+} ion.

The application of ion-solvent interactions to the processing of copper could lead to the development of low-energy and non-polluting processes to replace the conventional fire refining-electrorefining of crude copper. The acetonitrile-water solvent is only moderately corrosive compared to conventional acidic copper sulphate media. Cupric sulphate and acetonitrile can be recycled easily following thermal or electrochemical disproportionation of the cuprous sulphate. Elemental sulphur (for example when copper sulphide impurities are present) is a by-product, and most importantly, no metals other than copper are introduced into the processing solution. Several novel processes which have been advocated by Parker et al. are discussed below.

METALLURGICAL PROCESSES FOR COPPER IN ACETONITRILE/WATER MEDIA

Copper from Cupric Sulphate and Sulphur Dioxide

Sulphur dioxide is a desirable and readily available reductant for cupric salts, but in aqueous solutions reduction to copper occurs only at elevated temperatures and pressures and is usually incomplete. In the presence of acetonitrile, however, cupric sulphate solutions are reduced quantitatively to cuprous sulphate by SO_2 under ambient conditions and at pHs above 1 (14,18).

Copper from Copper-Lead-Silver Dross

A 1:1 acetonitrile/water solution containing sulphuric acid is a very powerful oxidizing agent capable of oxidizing both copper and silver (10). Reaction [4] occurs readily

$$Cu^{2+} + Cu^{o} \longrightarrow 2Cu^{+} \qquad [4]$$

$$Cu^{2+} + Ag^{o} \longrightarrow Ag^{+} + Cu^{+} \qquad [5]$$

at 25° and reaction [5] only somewhat less effectively. In this medium, silver is also cemented by copper according to reaction [6], whereas

$$Ag^{+} + Cu^{o} \longrightarrow Ag + Cu^{+} \qquad [6]$$

lead is unaffected because of its protective coating of lead sulphate (10). Thus an applciation for the removal of Cu and Ag from a blast furnace copper-lead-silver dross is suggested.

Copper from Copper-Lead Matte

Copper-lead matte derived from the drossing of lead bullion with sulphur contains many impurities, most notably As and Fe. The reactivity of the matte constituents to cupric sulphate in acetonitrile/water is $Cu_2S > PbS > CuS >> Pb$ (19).

$$Cu_2S + CuSO_4 \longrightarrow Cu_2SO_4 + CuS \quad [7]$$

$$CuS + CuSO_4 \longrightarrow Cu_2SO_4 + S \quad [8]$$

$$PbS + 2CuSO_4 \longrightarrow Cu_2SO_4 + PbSO_4 + S \quad [9]$$

$$Pb + S \longrightarrow PbS \quad [10]$$

$$Pb + 2CuSO_4 \longrightarrow Cu_2SO_4 + PbSO_4 \quad [11]$$

$$Cu_2SO_4 + \tfrac{1}{2}O_2 + H_2SO_4 \longrightarrow 2CuSO_4 + H_2O \quad [12]$$

Because these sulphides were attacked by redox reactions, no chemicals are consumed in the leaching processes. Other reactions to be considered in the leaching of copper-lead matte include those of lead with sulphur and with cupric sulphate and the oxidation of Cu(I) with oxygen. The recycling of covellite (CuS) was considered to be advantageous because it reacted preferentially

$$CuS + Cu_{(Pb)} \xrightarrow{\text{rapid}} Cu_2S \quad [13]$$

$$2CuS + Pb \xrightarrow{\text{slow}} Cu_2S + PbS \quad [14]$$

with copper to form mainly chalcocite which was highly reactive in the subsequent leaching operations. The rates and equilibria of the leaching of copper sulphides have also been studied (19). It appears that the extraction of metal impurities is in the order Zn $\simeq$ As > Fe > Ag.

Copper from Copper Sulphites via Chevreul's Salt

Copper concentrates can be sulphation roasted and leached with water to produce impure solutions of cupric sulphate. With careful control of the pH and the proportions of the reactants, Chevreul's salt ($Cu_2SO_3CuSO_3.2H_2O$) can be precipitated from aqueous cupric sulphate solutions with Na_2SO_3, $(NH_4)_2SO_3$ or $Mg(HSO_3)_2$. Copper ammonium

$$3CuSO_4 + 6NaHSO_3 \longrightarrow Cu_2SO_3CuSO_3.2H_2O + 3SO_2 + 3Na_2SO_4 + H_2SO_4 \quad [15]$$

sulphites ($Cu(NH_3)_4SO_3$) can also be precipitated when SO_2 is added to a solution of cupric sulphate in ammonia. The conditions for the formation and precipitation of the salts have been studied (20). It was found that sodium sulphite was more effective than the same molar proportion of ammonium sulphite for precipitating copper sulphite from dilute cupric sulphate solutions. Precipitation at 75° was more effective (90% at pH 3) than at 25°. Small amounts of iron(II)- and zinc sulphites coprecipitated with the Chevreul's salt. To eliminate these elements, purification was done by washing with sulphurous acid at pH 2-3 after the precipitate had formed. Copper was recovered by dissolution of the Chevreul's salt with $CuSO_4$/acetonitrile/water and thermal disproportionation of the resulting cuprous sulphate solution. Copper ammonium sulphites were preferably converted to copper sulphite with separation of $(NH_4)_2SO_4$ before leaching with $CuSO_4$/acetonitrile/water.

Separation of Copper and Nickel

The above methods were also found suitable for the separation of copper from nickel in aqueous solutions (20-22). Such solutions are commonly produced in the nickel processing industry, and traditionally have been difficult to purify by conventional methods (for example, with H_2S

precipitation of CuS). Copper sulphite was precipitated as Chevreul's salt from solution using nickel bisulphite. When the precipitation was done from 0.5 M $CuSO_4$ and 0.5 M $NiSO_4$ with equimolar $Ni(HSO_3)_2$ at pH 2.9, 96-98% of the copper was precipitated and the Chevreul's salt contained 1-3% Ni. This purity was considered acceptable for subsequent dissolution in $CuSO_4$/ acetonitrile/water followed by thermal disproportionation since nickel is left in the aqueous solution after distillation of the acetonitrile. The copper-free nickel sulphate solution could be converted to nickel by conventional procedures; e.g., electrowinning.

Copper from Chalcopyrite

Chalcocite (Cu_2S) and digenite are the most readily leached copper sulphides. Chalcocite is only slightly soluble in 1 M aqueous H_2SO_4 (solubility product at 25° is 10^{-25}), but in anhydrous acetonitrile containing 1 M H_2SO_4 the solubility product (equation [16]) is 10^{40} (10).

$$Cu_2S + 2H^+ \longrightarrow 2Cu^+ + H_2S \qquad [16]$$

The reaction of chalcopyrite with sulphur results in the formation of covellite (equation [17]), idaite (equation [18]) or bornite (equation [19]) (23).

$$5CuFeS_2 + 5S \longrightarrow 5CuS + 5FeS_2 \qquad [17]$$

$$5CuFeS_2 + 4S \longrightarrow Cu_5FeS_6 + 4FeS_2 \qquad [18]$$

$$5CuFeS_2 + 2S \longrightarrow Cu_5FeS_4 + 4FeS_2 \qquad [19]$$

A characteristic of the above reactions is that the copper sulphides are intimately associated with pyrite. Physical separation of the minerals after roasting was impractical and recourse was made to the selective dissolution of copper from the pyrite. The relative reactivity of these sulphides towards

$CuSO_4$/acetonitrile/water is: bornite > covellite > idaite (23). As copper was extracted from the sulphides, the residue became progressively more difficult to leach and, hence, more demanding conditions of concentration, temperature and pulp density were required. Countercurrent leaching was suggested for bornite in this medium. Although 80% of the copper was readily leached at 60°C, a little iron was found in the leaching solution after even modest copper dissolution. Most of the iron in the bornite did not report to the solution, however, until over 70% of the copper had been leached. A comparison of the leaching of bornite in this medium, in $CuCl_2$/NaCl/water and in $Fe_2(SO_4)_3/H_2SO_4$/water has been discussed (23). A redox equilibrium between cuprous sulphate, cupric sulphate and partially leached solid copper sulphide, Cu_xS, where x = 0 to 2, has been established (24). The equilibrium concentration of cuprous sulphate and the value of x in Cu_xS, in solutions saturated with $CuSO_4$, were interdependent if the acetonitrile concentration was constant. This behaviour was considered in terms of the structural and electrochemical changes occurring in the Cu_2S and CuS as the leaching proceeded. Depending on the concentrations of acetonitrile, cuprous sulphate and cupric sulphate, CuS was either oxidized by cupric sulphate to a less copper-rich sulphide or even to sulphur, or reduced by cuprous sulphate to a more copper-rich sulphide, up to Cu_2S.

Chalcopyrite could also be reduced by copper(I) solutions to chalcocite and bornite while the iron reported to the solution (25). Factors which affect the rate and efficiency of reduction were examined. The reduction was rapid on fresh chalcopyrite surfaces, and high concentrations of Cu^+ in the presence of copper and Cu^{2+} were necessary to drive the reduction to completion. Reactions in the presence of copper metal (Equations [20], [21]) were

$$CuFeS_2 + Cu^o + 2Cu^+ \longrightarrow 2Cu_2S + Fe^{2+} \quad [20]$$

$$CuFeS_2 + 2Cu^o + Cu^{2+} \longrightarrow 2Cu_2S + Fe^{2+} \quad [21]$$

more effective than reaction with Cu^+ only (Equation [22]) in acidified

$$CuFeS_2 + 4Cu^+ \longrightarrow 2Cu_2S + Fe^{2+} + Cu^{2+} \quad [22]$$

acetonitrile/water. Reduction with copper metal in acidified water at 100° was the most effective method of converting the chalcopyrite to Cu_2S.

The main disadvantage of the above leaching processes was the presence of iron in the resulting solution of copper(I). Obviously, thermal disproportionation was not a wise route to recover the copper from the pregnant cuprous sulphate solution. It was suggested to electrolyze the solution in a diaphragm cell to give copper cathodes and cupric sulphate solution (26,27) for recycle. Separation of the iron and copper before thermal disproportionation is necessary and will be discussed in a later section.

In the dead roasting of chalcopyrite, any sulphur remaining was associated with copper as digenite ($Cu_{1.8}S$), covellite (CuS) or the basic sulphate, $CuOCuSO_4$. In the acetonitrile leaching process, the presence of retained sulphur in the calcine has a detrimental effect (28,29). Experiments to recover copper from a sulphide concentrate containing iron as well as one containing nickel and iron have also been reported (29).

Copper from Segregation-Roasted Concentrates

The main problem in refining segregation-roasted concentrates was the separation of copper from iron. Suppression of iron dissolution required a good knowledge of the E_h-pH diagram for the copper and iron species involved (30). The higher the E_h of the solution, the lower the pH at which iron first enters the solution. During leaching of calcines containing

magnetite and copper, using $CuSO_4$/acetonitrile/water as the oxidant, a high E_h was achieved with a high concentration of Cu^{2+} ions and a low activity of Cu^{+} ions by the control of the concentration of copper ions or the proportion of acetonitrile in the solvent (31). At high E_h (>0.5 V) and high pH (>3), reaction [22] disposed of any iron(II) present in the

$$2CuSO_4 + 2FeSO_4 + 3H_2O \longrightarrow Fe_2O_3 + Cu_2SO_4 + 3H_2SO_4 \qquad [23]$$

leach solutions. Supression of soluble iron from magnetite was achieved by dissolution of $FeSO_4$ (equation [24]) followed by its

$$Fe_3O_4 + H_2SO_4 \longrightarrow FeSO_4 + Fe_2O_3 + H_2O \qquad [24]$$

precipitation as Fe_2O_3 (equation [23]). Thus after treating a copper-free magnetite with 0.5 M $CuSO_4$ in 6 M acetonitrile at 55° and pH 3 for one hour, no change in the magnetite was detected (30). A condition was identified whereby 92-98% of the copper was extracted into 6 M acetonitrile with less than 0.07 M iron dissolution from a double-roasted calcine. The copper-rich calcine was first leached at pH 3.5 with 1 M $CuSO_4$ to give 0.9 M Cu_2SO_4 and 0.1 M $CuSO_4$ at a final E_h <0.4 V. The copper-rich residue was then leached at pH 2.5 with 1 M $CuSO_4$ to give a solution of 0.2 M Cu_2SO_4 and 0.8 M $CuSO_4$ at E_h >0.5 V.

Calcines containing much lead gave the lowest copper recoveries. Copper and silver may dissolve in molten lead during segregation and thereby become inert to the $CuSO_4$/acetonitrile/water leaching solution.

Separation of Iron(II) and Copper(II)

In hydrometallurgical solutions containing iron(II) and copper(II), it is usually necessary to extract or to precipitate iron from

the solution. Equilibrium [25] lies well to the left in water (log K = -10.5),

$$Cu^{2+} + Fe^{2+} \xrightarrow{K} Cu^{+} + Fe^{3+} \qquad [25]$$

but the equilibrium is shifted to the right by the addition of Cl^- or acetonitrile due to the formation of $Cu(CH_3CN)_3^+$ and $FeSO_4^+$ complexes. Log K was about -2.5 in 4 M NaCl or acetonitrile allowing iron to be removed selectively from copper(II) solutions by either solvent extraction with versatic acid or precipitation as goethite or jarosite (31,32). This approach was suited to concentrated solutions of Cu(II) and Fe(II), and yielded concentrated iron-free solutions of Cu_2SO_4 or CuCl. The equilibrium constant for reaction [25] has been measured over a range of NaCl concentrations and compared with values in acetonitrile. The practical application, however, depends on the E_h and pH of the solution. Of particular concern are the stability regions of Cu(I) as $Cu(CH_3CN)_3^+$ or $CuCl_2^-$, of Fe(III) as $Fe(OH)_3$, goethite or jarosite, of basic copper chlorides and of basic copper sulphates. The stability of Cu(I) was determined largely by the concentration of Cl^- or acetonitrile, and the form of the Fe(III) precipitate mostly was controlled by the temperature. Jarosite and goethite were precipitated only at temperatures above 80°. The E_h-pH diagram for the Cu-Fe-water-acetonitrile-SO_4^{2-} system has been applied to the leaching of a segregation-roasted calcine of chalcopyrite. The calcine, which contained ∿35% Cu(0) and 40% Fe_3O_4, was leached first with Cu(II)/acetonitrile/water at pH 3.5 and E_h 300-400 mV to dissolve Cu(0) but not Fe_3O_4. High concentrations of $Cu(CH_3CN)_3^+$ were produced, but some basic copper sulphates precipitated and remained with the magnetite residue. A second leach, at pH 2.5 and E_h 400-500 mV, dissolved the remaining copper and basic copper sulphates. Good E_h and pH control were required to prevent the dissolution of magnetite

or $Fe(OH)_3$. Magnetite dissolves readily at pH 2.5 and Eh 300-400 mV, but not at Eh 500-600 mV and pH 2.5.

A study of iron extraction using versatic acid in Escaid-100 for a solution of 0.1 M Cu(II) and 0.1 M Fe(II) in 3 M NaCl acetonitrile/water has been carried out (32). Versatic acid selectively extracted iron as Fe(III) at $pH_{\frac{1}{2}}$ = 3.4 from 6 M acetonitrile before the extraction of Cu(II) at $pH_{\frac{1}{2}}$ = 4.9. Cu(I) was not extracted. In the absence of acetonitrile, Cu(II) was extracted at a similar pH but before Fe(II) at $pH_{\frac{1}{2}}$ = 5.7. Acetonitrile has little effect on the solvent extraction of Cu(II) and Fe(II) because these ions are preferentially solvated by water in dilute acetonitrile. Thus by the addition of acetonitrile in Escaid-100, it is possible to extract iron selectively by solvent extraction with versatic acid and then recover the acetonitrile and copper by distillation. Less than 5% acetonitrile transfers into the organic phase from which it can be readily stripped with water.

Precipitation of iron as goethite from concentrated Cu(II) and Fe(II) solutions has been attempted by the addition of acetonitrile and base (MgO) (32). The necessary low concentrations of Fe(III) were achieved by continuous displacement of equilibrium [25]. By adding NH_3/acetonitrile to $CuSO_4$-$FeSO_4$ solution, slightly less iron was recovered from solution as jarosite than as goethite because the final concentration of Fe(III) in solution was high. When jarosite was precipitated by the addition of acetonitrile and NH_3 to more concentrated solutions, between 56-91% of the iron was precipitated at pH 2.5-3 as a readily filterable crystalline solid. It was found that sufficient NH_4^+ was present from acetonitrile hydrolysis to give ammonium jarosite. The amount precipitated depends on the final concentration of acetonitrile in solution. High concentrations

favour a displacement of equation [25] to the right. The jarosite precipitate was more readily filterable than $Fe(OH)_3$ and contained less entrained copper (1-2%).

Kinetics of Oxidation of Fe(II) Catalyzed by Cu(II)

In the absence of Cu(II), Fe(II) was oxidized to Fe(III) very slowly and at similar rates in water, in 6 M acetonitrile or in 4 M NaCl. By contrast, it was found that the rate of oxidation of $Cu(CH_3CN)_3^+$ and $CuCl_2^-$ in 6 M acetonitrile and 4 M NaCl, respectively, was about 1000 times faster than the rate of oxidation of Fe(II) in water (32). The rate of oxidation of Cu(I) depended on the concentration of Cu(I) and, hence, the concentration of acetonitrile or Cl^- as well as pH. The catalytic effect of Cu(II) in water was relatively small. In the presence of 4 M NaCl or 6 M acetonitrile the same concentration of Cu(II) increased the initial rate of oxidation of Fe(II) by a factor of 100 relative to that in water. The rate of oxidation of Fe(II) fell as the concentration of dissolved Fe(III) increased, with the inhibition by Fe(III) being most significant at low concentrations of acetonitrile or Cl^-.

Extraction of Copper(I)

Several hydrometallurgical processes such as the leaching of scrap copper, chalcopyrite or sulphur-activated chalcopyrite with Cu(II)Cl in brine result in solutions of Cu(I)Cl. The copper is solubilized as complex anions such as $CuCl_2^-$ or $CuCl_3^{2-}$. Direct leaching of chalcopyrite with stoichiometric quantities of $FeCl_3$ also produces $CuCl_2^-$ (equation [26]).

$$CuFeS_2 + 3FeCl_3 \xrightarrow{MCl} CuCl_2^- + 4FeCl_2 + 2S \qquad [26]$$

(MCl = inert, soluble chloride)

Copper recovered from such processes is invariably contaminated with iron, as well as lead, silver, arsenic, antimony and bismuth. Several preliminary studies of the recovery of copper have been reported; for example, crystallization of CuCl by cooling the leach liquor (33); precipitation of a butadiene-CuCl adduct at low temperatures and regeneration of the butadiene by heating to 60°C (34); oxidation of copper(I) to copper(II) chloride prior to extraction with LIX 65N (35); extraction of copper(I) using trialkyl phosphite (36); extraction with tri-n-butyl phosphate or quarternary amine chlorides (37); and, finally, direct extraction and recovery of copper(I) chloride using organic nitriles (37).

Organic nitriles complex with CuCl to form soluble complexes of $Cu(RCN)_3Cl$. Copper complexed with benzonitrile oxidized to copper(II) chloride in the organic phase prior to stripping with water. When acetonitrile was used, CuCl could be recovered in a pure form by distilling the volatile nitrile (37). Because acetonitrile is miscible in all proportions with water, it can be used in aqueous leach liquors containing up to 2 M dissolved salts ($FeCl_2$ or NaCl) without the danger of salting-out acetonitrile-rich organic phases. This method has been applied to the recovery of pure copper(I) chloride from chalcopyrite concentrates leached with iron(III) and copper(II) chlorides. The purity of the recovered copper(I) chloride suggested that electrolytic grade copper could be obtained by reduction with hydrogen.

The distribution coefficients of Na^+, Cu^+, Cu^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+} and Fe^{3+} chlorides between aqueous sodium chloride solutions and acetonitrile-water have been measured (37). An increase in the concentration of NaCl in the presence of 0.5 M HCl rendered acetonitrile less soluble in the aqueous phase. By contrast, increasing the concentration of HCl in the

presence of 2 M NaCl enhanced the solubility of acetonitrile in the aqueous phase. Although copper(I) chloride was present in the aqueous phase as $CuCl_2^-$, $CuCl_3^{2-}$, etc. anions, it was apparent that copper(I) chloride was present mainly as the monochloride in the organic phase. Significantly, the distribution coefficient for copper(I) increased slightly as the aqueous NaCl concentration increased, but decreased as the aqueous HCl concentration increased. Therefore, the order of extractability of copper(I) chloride into the acetonitrile phase was $CuCl \gg H^+CuCl_2^- > Na^+CuCl_2^-$. The optimum composition of the aqueous phase was 2 to 4 M NaCl/0.5 M HCl. Successive extractions with acetonitrile from a solution of 3 M $FeCl_2$, 1 M NaCl, 0.5 M HCl and 0.4 M CuCl enabled more than 95% of the copper(I) to be extracted in three contacts. Countercurrent extraction was proposed and the equilibrium isotherm has been studied (37).

Changes in equilibrium [27] have also been studied (37) as acetonitrile was added to water

$$CuCl_2 + FeCl_2 \rightleftharpoons CuCl + FeCl_3 \qquad [27]$$

Although significant amounts of copper(II) chloride and iron(II) chloride were not individually extracted into the acetonitrile phase, appreciable amounts of both copper and iron were extracted from solutions of $CuCl_2$ and $FeCl_2$ in aqueous chloride solutions because equilibrium [27] produced copper(I) and iron(III) chlorides. In the presence of a large excess of iron(II) chloride and in the absence of iron(III) chloride, all copper initially present as copper(II) chloride was extracted into acetonitrile together with an equivalent amount of iron. The ratio of Fe/Cu in the organic phase was 1.15. Copper was extracted as copper(I) chloride and iron as iron(III) chloride. Equilibrium [27] was shifted strongly to the right with the addition of acetonitrile. Therefore, leach

solutions which contained $CuCl_2$ and CuCl in the presence of $FeCl_2$ caused iron to be extracted into the acetonitrile phase. When the acetonitrile was distilled, equilibrium [27] shifted to the left and equimolar concentrations of Cu^{2+} and Fe^{2+} remained in the aqueous phase. This resulted in low yields of CuCl. For this reason, it was necessary to optimize the concentration of CuCl relative to that of $CuCl_2$ in the leach solution prior to nitrile solvent extraction. This was accomplished by a two-stage counter-current leach. In the first stage, Cu^{2+} was reduced with fresh chalcopyrite, and the resulting leach solution contained 90% of the copper as copper(I) chloride. Following the two-stage leach, the pregnant liquor was treated with cement copper to convert the remaining 10% copper(II) to copper(I). The copper(I) chloride complex was then extracted in a three-stage counter-current system with acetonitrile. Distillation of the organic phase recovered the acetonitrile and pure CuCl precipitated from the aqueous phase together with soluble iron species and any Cu^{2+} species present. The reagents 2-hydroxy cyanoethane and acrylonitrile have also been employed (38) in place of acetonitrile.

This approach has also been applied for the separation of copper(I) chloride from leach solutions arising from a chlorination roast of nickel matte (39). The following nitriles were used: acetonitrile, propionitrile or 3-hydroxy-propionitrile which gave solubility relationships similar to those of CuCl.

Purity of the Copper Powder

Of the mixed solvents studied, the acetonitrile/water system appears most promising, and certainly is the most extensively studied. The use of the acetonitrile/water mixed solvent to obtain pure copper from copper-

bearing materials is a rapid, low energy and low capital process. The recovery of copper electrolytically from the mixed solvent leads to solvent losses. Precautions must be taken to exclude air and to contain volatile nitrile vapours (26). For these reasons, copper recovery via thermal disproportionation using low grade steam is emphasized in the present report.

Table I summarizes the results obtained from the application of the acetonitrile/water leach with subsequent thermal disproportionation on the purity of the copper powder. Although good quality copper is obtained, compared to the composition of commercial copper cathode, the impurity levels found are sometimes relatively high. Solution pretreatment and precipitation of As, Sb and Bi are required to obtain a high quality copper powder. For example, the addition of iodide ion gives insoluble BiOI and SbOI (26). There are several conditions necessary to obtain iron-free copper powder. The dissolution of iron during leaching with solvent acetonitrile/water (30) must be minimized. The conditions for minimizing the amount of iron entering the solution have been reported and related to the Eh-pH relationships for the copper and iron species. These conditions have been established and have been applied to the recovery of copper from segregation-roasted copper concentrates. The level of iron in the copper product is within the range of commercial copper cathode (Table I, column 11) (30). When copper is recovered via Chevreul's salt, the factors governing the formation and precipitation of Chevreul's salt must be considered to prevent small amounts of iron(II) sulphite (also zinc sulphite) from being coprecipitated with the Chevreul's salt (20). Iron levels in the product are shown in Table I, columns 12, 13. They are at the upper limit of the range for commercial cathode copper.
These facts may have led previous investigators to separate iron from

Table I. Comparison of the purity of copper made from mixed solvent systems with that of commercial cathode copper (in ppm)

Element	Industrial Cathode Compositions[a]	Using Acetonitrile/Water and Thermal Disproportionation													
		1[b*]	1[b**]	2[c]	3[c]	4[c]	5[c]	6[c]	7[c]	8[d]	9[e]	10[f*]	11[f*]	12[g]	13[g]
Ni	<7	<0.1	<5	0.1	0.88	0.1	ND	<5	<5	<0.5	4	<0.1	<0.1		
Pb	<5	<0.1					ND			<10	5	<0.1	0.34		
As	<1	0.2		187	0.37	0.42	0.5			8-22	0.2	0.5	<0.1		
Sb	<2	0.1		166	0.53	3.6	12[h]			<5		12[h]	0.16		
Se	<1						ND					<0.1			
Fe	2-6	0.2	<5				0.6	<5	<5	10	16	0.6	<10=DL	10	<5
Te	<1														
S	4-7														
Bi	<3	<0.1		31	0.26	2.86	ND			<5	10	<0.1			
Ag	5-10	0.8					1.3			<2	20	1.3	<1		
Au	0-0.1														
Zn			4					4	<5	20	5		6	<5	4
Co							ND				2	<0.1	6=DL		
Sn							ND			<50		<0.1			
Cd										<0.5					
Ca													0.7		
K															
Mg			7					7	<5					<5	7
Year Published		1976	1976	1977	1977	1977	1977	1977	1977	1979	1980	1981	1981	1981	1981

FOOTNOTES FOR TABLE I

1) Copper powder from atomized blister copper.

2) Copper powder after leaching copper-arsenic sludge residues from the Townsville Copper Refineries tankhouse with Cu_2SO_4/acetonitrile/water at pH >2 without solution pretreatment

3) As 2 but with proprietary solution pretreatment and precipitation of As, Sb, and Bi.

4) As 3 but leached at pH <2.

5) Copper powder resulting after leaching three batches of doubly-roasted chalcopyrite calcine supplied by Amax.

6) Copper powder from impure $CuSO_4$ solutions recovered via Chevreul's salt.

7) Copper powder from a synthetic $CuSO_4$-calcined Fe_2O_3 mixture and recovered via Chevreul's salt.

8) Copper powder from copper-lead matte.

9) CuCl product via direct extraction and recovery using acetonitrile in the presence of chloride salts.

10) Copper powder from double roasted chalcopyrite.

11) Copper powder from TORCO segregated copper.

12) Copper powder via Chevreul's salt by addition of $(NH_4)_2SO_3$ to 1 M $CuSO_4$, and subsequent dissolution of Chevreul's salt in $CuSO_4$/acetonitrile/water.

13) As in 12, but dissolution of Chevreul's salt in impure $CuSO_4$/ acetonitrile/water.

Footnotes for Table I (continued)

a) Biswas, A.K. and Davenport, W.G., Extractive Metallurgy of Copper, 295-323, Pergamon Intern., Oxford, 1976.

b) Reference 18.

c) Muir, D.M. and Parker, A.F., Adv. in Extr. Metall. (Inst. Min. Metall., London), 191-195 (1977).

d) Reference 19.

e) Reference 37.

f) Reference 30.

g) Reference 20.

h) Believed to be due to inefficient filtration. Powder from first recycle contained 1.4 ppm Sb.

* Analyzed by mass spectrometry.

** Analyzed by atomic absorption spectrometry.

DL = Detection limit

ND = Not Detected

the copper(I) leaching solution prior to thermal distillation of the acetonitrile (31,32). When extraction of iron with versatic acid is used, the stability region of Cu(I) as $Cu(CH_3CN)_3^+$, determined by the concentration of acetonitrile, is found to be important (32). When the separation is based on precipitation of the iron, the stability regions of $Fe(OH)_3$, goethite, or jarosite are important and are determined by the temperature, Eh and pH of the solution. Another important factor is the catalytic effect of Cu(II) on the oxidation of Fe(II) to Fe(III) in 6 M acetonitrile that is enhanced by 10^2 times compared to water (32). Although the conditions for the extraction of iron using versatic acid and the precipitation of goethite or jarosite have been studied (32), no report has appeared on the application of this technology. Therefore, no data exist for the purity of the copper powder resulting from these separations.

Data resulting from the recovery of copper from copper-lead matte are listed in Table I, column 8. Although the reactivity of the matte constituents towards cupric sulphate in acetonitrile/water is Cu_2S > PbS > CuS >> Pb (19), the level of Pb in the copper product is higher than in the commercial cathode copper. The same is true for other impurities; i.e., As, Fe, Ag and Sn.

It is troublesome to have different process conditions for each type of crude copper and to require different purification processes for each impurity. It would be ideal if copper(I) could be extracted into the acetonitrile leaving behind all the metal impurities in the aqueous phase. This has been attempted using direct extraction and recovery of copper from chalcopyrite with acetonitrile/water in the presence of $CuCl_2$ and $FeCl_3$ (37). The acetonitrile phase solvates the CuCl; the impurity salts are solvated by the aqueous phase. After separation of the two layers and distillation

of the acetonitrile, the resulting CuCl contains Fe and Ag in amounts above the range found in commercial cathode copper (Table I, column 9). It has been established that although copper(II) and iron(II) chlorides are not significantly extracted individually be acetonitrile, iron(III) chloride is extracted with its distribution coefficient being slightly higher than that of Cu(I) chloride. In the presence of Cu(II)-, Fe(II)-, Cu(I)- and Fe(III) chlorides, acetonitrile shifts the equilibrium $Cu(II) + Fe(II) \rightleftarrows Cu(I) + Fe(III)$ to the right. The two-stage leaching method (37) optimises the concentration of CuCl and drives the equilibrium to the left, therefore suppressing the amount of Fe(III) as shown in Table I, column 9.

There is no reported explanation as to why the silver level in the CuCl product is high (37). It is likely that silver in chalcopyrite is leached by $CuCl_2$ and $FeCl_3$ forming silver chloride. Silver chloride is slightly soluble in water, and its solubility in the brine solution is increased slightly (40). In the presence of chloride ion and acetonitrile, however, the equilibrium $AgCl + Cl^- \rightleftarrows AgCl_2^-$ is shifted to the right. Acetonitrile is a moderately good solvator for $AgCl_2^-$ relative to water (40). Therefore, $AgCl_2^-$ enters into the acetonitrile layer during the extraction process. It has been found that silver metal can be extracted with Cu(II) sulphate/acetonitrile/water containing significant concentrations of Cu(I) sulphate (30). Whether the same is true in Cu(I) chloride/acetonitrile/water media containing significant amounts of Cu(I) chloride has not yet been determined. Although the distribution coefficients for the extraction of a number of metal chlorides into acetonitrile in the presence of NaCl and HCl have been obtained, no such study for silver chloride has been reported.

From the above review and interpretation of published studies, it appears that the extraction of the copper(I) species followed by the thermal distillation of the acetonitrile is a promising means of obtaining pure copper powder. A better extraction method needs to be developed, however, to reduce the impurities in the copper product.

Separation of Cations by Ion-Exchange

Several workers have studied the effect of non-aqueous solvents on the separation of metal chloride mixtures by ion exchange (41-43). Aqueous acetonitrile promoted the formation of $CuCl_3^-$, $CoCl_4^{2-}$ and $NiCl_4^{2-}$, and increased the metal loadings on the resin (44). Aqueous dimethylformamide showed more diverse loading characteristics. The loading of $ZnCl_3^-$, $FeCl_3^-$, $PbCl_3^-$ and $CoCl_4^{2-}$ decreased in concentrated dimethylformamide solution. There was no evidence of $NiCl_4^{2-}$ formation in dimethylformamide as occurs in acetonitrile.

METALLURGICAL PROCESSES FOR SILVER IN ACETONITRILE/WATER OR DIMETHYL SULPHOXIDE/WATER MEDIA

Direct Leaching of Silver from Segregation-Roasted Calcines

Leaching tests established that silver metal was not dissolved and extracted by $CuSO_4$ in 6 M acetonitrile/water solutions at Eh values below 0.5 V and containing significant concentrations of $CuSO_4$.

$$2CuSO_4 + 2Ag \longrightarrow Ag_2SO_4 + Cu_2SO_4 \qquad [28]$$

Silver was leached by $CuSO_4$/acetonitrile/water only when the Eh values were above 0.5 V (30). Such Cu^{2+}/Cu^+ redox potentials were achieved in 6 M acetonitrile/water-saturated $CuSO_4$ by maintaining the concentration of Cu^+ <1 g/L or in 10 M acetonitrile/water by maintaining the concentration

of Cu^{+} <10 g/L. Thus it was possible to leach copper selectively from a segregation-roasted calcine using $CuSO_4$/6 M acetonitrile/water, and then leach silver metal from the residue using $CuSO_4$/10 M acetonitrile/water (30). Unlike silver metal, silver sulfide was not extracted under these conditions. It was, however, extracted by excess cyanide under oxidizing conditions. Because Ag_2S was present in several of the calcines after leaching, the following procedure was followed. More than 99% of the copper was extracted by leaching with Cu^{2+}/acetonitrile/water, followed by the leaching of the washed residue with NaCN/water to recover >90% of the silver (45). Gold values in the calcines were low, but 80% of the gold was also extracted during cyanidation.

Silver from Crude AgCl

Materials containing Ag in a form which can be converted to AgCl include anode slimes leach residues, silver halide leaching residues and AgCl cakes from gold refining (40). Equilibria [29] and [30]

$$AgCl \underset{}{\overset{K_{So}}{\rightleftharpoons}} Ag^{+} + Cl^{-} \qquad [29]$$

$$AgCl + Cl \underset{}{\overset{K_{S2}}{\rightleftharpoons}} AgCl_2^{-} \qquad [30]$$

lie strongly to the left in water so that silver chloride is only slightly soluble at 25° (pK_{So} = 9.8). Silver chloride is exceptionally soluble at 25° when dissolved in dry dimethyl sulphoxide containing excess $CaCl_2$. When 30-40% H_2O by volume was added to the solution, pure silver chloride was precipitated almost quantitatively. It could then be converted to pure Ag metal by melting at 1100° with excess Na_2CO_3, by reduction with hydrogen at 300-400°, or by reduction of an aqueous suspension with zinc dust.

Silver and Gold from their Sulphides, Selenides and Tellurides

Oxidative leaching of silver and gold from sulphides, selenides and tellurides was done using $CaCl_2$ in dry dimethyl sulphoxide containing $CuCl_2$ at 80°C. Water was added to precipitate AgCl and Au (46). The resulting residue contained elemental sulphur and small amounts of unreacted Ag_2S.

METALLURGICAL PROCESSES FOR GOLD IN ACETONITRILE/WATER MEDIA

Activated carbon is widely used to adsorb gold from dilute aqueous cyanide solutions. Sodium cyanide in 40% acetonitrile/water is able to desorb large quantities of gold from activated carbon under ambient conditions (47). The strong desorption in the presence of acetonitrile was a consequence of several factors (48) which influence equilibrium [31].

$$AuCN_{(carbon)} + CN^-_{(aq)} \overset{K}{\rightleftharpoons} Au(CN)_2^-{}_{(aq)} \qquad [31]$$

Acetonitrile is more strongly adsorbed on carbon than is water. Adsorption of acetonitrile decreases the affinity of carbon for AuCN. Furthermore, CN^- is more strongly solvated in 40% acetonitrile/water than in water, whereas $Au(CN)_2^-$, with gold present as a d^{10} Au^+ species, is more strongly solvated by acetonitrile/water than by water. Consequently, the distribution coefficient for reaction [31] favours desorption of gold in 40% acetonitrile/water by a factor of 10^4 over its value in water at 25°C. The kinetics and loading of gold on carbon have been determined to be dependent on temperature, pH, ionic strength and other complex ion effects (49-51).

OTHER TYPES OF MIXED SOLVENTS

Because of the successful research in the application of nitrile solvents in hydrometallurgy, several workers have shown an interest in applying different mixed solvents (52-57) to metallurgical problems. Pyridine/chloroform mixtures were used to leach copper from copper-bearing sulphidic materials (52,53). Pyridine (Py), especially in the protonated form, forms complexes with copper(II) chloride according to equations [32,33].

$$CHCl_3 + Py \longrightarrow PyH^+ + Cl^- + :CCl_2 \qquad [32]$$

$$Cu_2S + 4PyH^+ + 4Cl^- + O_2 \xrightarrow{Py} 2CuCl_2Py_4 + S + 2H_2O \qquad [33]$$

The protonated pyridine was present in equilibrium with the solid complex of copper(II) chloride, $CuCl_2Py_2$. The leaching of chalcocite in this medium resulted in 100% copper recovery after 1 hour, with about 90% recovery occurring during the first 30 min (54). The rate of chalcocite dissolution was higher in the pyridine/pyridine.HCl system than in the pyridine/chloroform system. Thorough studies of the effects of contaminants as well as the influence of $:CCl_2$ species during leaching have not yet been done. Because of the lone pair of electrons in $:CCl_2$, this species may be regarded as reactive. It was suggested that the copper be stripped with water followed by the extraction of some of the dissolved pyridine using chloroform. Recovery of copper after stripping could be done by electrowinning or cementation.

Sulphur dioxide in dimethyl sulphoxide is a potentially useful leaching medium for metals and oxides (55,56). Further study (57) showed that metals such as Mg, Al, In, Sn, Ti, V, Mn, Fe, Co, Ni, Cu, Zn and Cd react with this mixed solvent to form metal disulphates, whereas Sr, Ba

and Pb react to form metal sulphates. Other metals, such as Li, Na, Be, Ca, Ga, Tl, Sb, Bi, Ce, Pr, Eu, Dy and U dissolve in the mixed solvent to give products that have not yet been characterized. The mechanisms of formation of these products have not been elucidated, but may involve a reaction which proceeds via the $[SO_2]^-$ radical ion and ion-pairs containing a metal ion and $[SO_2]^-$.

FORMATION OF METAL SALT-SOLVENT COMPLEXES

Cations such as Ag^+ and Cu^+ are solvated by acetonitrile (CH_3CN) in acetonitrile/water, whereas other ions like NO_3^- and ClO_4^- are selectively solvated by water in the solvent mixture (58). These observations have formed the basis of potential applications to copper and silver hydrometallurgy (11,59). Therefore, the understanding of the formation of cation-solvent complexes is important.

Pawelka (60) reported a value of four for the stability constant of $Ag(CH_3CN)^+$ determined by potentiometry. Koch also employed potentiometry to study the formation of $Ag(CH_3CN)_2^+$ in water. The stability constant of the diacetonitrile complex determined at different ligand concentrations, however, varied by a factor of over 30 (61). Manahan and Iwamoto doubted if silver species other than the diacetonitrile complex were present in the solution. Using potentiometric titration of solutions of silver perchlorate ($AgClO_4$) with solutions of acetonitrile, however, they found the highest silver complex to be $Ag(CH_3CN)_3^+$ (62). Parker et al., using potentiometric and conductivity methods, concluded that $Ag(CH_3CN)_2^+$ existed in acetonitrile/water, 2-hydroxycyanoethane/water, or pyridine/water solutions in their studies of the transfer of single ions from water to the organic solvent (63,64). Schneider (65) employed a combination of electrochemical methods and NMR spectroscopy for the investigation of ion

solvation. He believed that the two different methods would perceive the region around an ion differently. While NMR is sensitive to the environment directly surrounding the nucleus of an ion, electrochemical methods are sensitive to the interaction of an ion with species outside the primary solvation shell. Although NMR has the disadvantage of being less sensitive relative to electrochemical methods, it offers more comprehensive information about the solvation of charged ions. For a number of ions, the lifetime of solvent molecules in the primary solvation shell is relatively long ($>10^{-3}$-10^{-4} s). Under favourable conditions in mixed solvents, it is possible to observe separate resonance lines for all cationic species that differ with respect to the composition of their primary solvation shells. By observing the proton chemical shift of dimethyl sulphoxide in solutions of $AgClO_4$, Schneider et al. found four coordination numbers for Ag^+ with dimethyl sulphoxide (66).

Potentiometry suggested a maximum of four acetonitrile molecules in coordination with copper(I) ions. Compounds such as $Cu(CH_3CN)_4ClO_4$ and $Cu(CH_3CN)_4NO_3$ have been isolated (62). In sulphate solutions of high ionic strength, Parker et al. suggested the highest copper(I)-acetonitrile complex to have the formula $Cu(CH_3CN)_4^+$ (69). The specific conditions yielding the $Cu(CH_3CN)_3^+$ complex were not reported (63,64,67). It is also believed that a decrease in conductivity during the course of electrowinning of copper(I) in dimethyl sulphoxide ($(CH_3)_2SO$) solutions is attributable to the formation of larger, less mobile complexes such as $Cu[(CH_3)_2SO)]_6^{2+}$ (68). In the $CuCl_2$-acetonitrile system, it has been found spectropotometrically that the concentrations of the $CuCl_3(CH_3CN)^-$ and $CuCl(CH_3CN)_3^+$ ions increased with the composition of the coordination sphere and redox properties of the chloro copper(II) complexes (70).

Several proton and N-14 NMR studies have been attempted to determine the kinetic parameters characterizing the exchange of solvent molecules between the first coordination sphere of transition metal ions (Cu^{2+}, Ni^{2+}, Co^{2+}, etc.) and the bulk solvent (71-74).

A thermodynamic study of CoX_2 (X = Cl, Br) in acetonitrile or propionitrile at 21-107°C has been done using the equilibrium decomposition pressure method. Two stoichiometric compounds were identified: $Co(RCN)_3X_2$ and $Co(RCN)_2X_2$ (75). A method based on line broadening of the proton NMR spectrum has been described for finding the fraction of the solvation shell of a paramagnetic solute occupied by a given solvent in a mixed solvent system. This method has been applied to the Co^{2+} or Ni^{2+} dimethylformamide/water and dimethyl sulphoxide/water systems (76).

Aluminum chloride in mixtures of dimethyl sulphoxide/water has also been studied by proton NMR. The measurements of the rate of exchange of dimethyl sulphoxide molecules between coordinated and bulk solvent sites suggested that dimethyl sulphoxide molecules could exchange via two mechanisms. The first was the direct exchange of dimethyl sulphoxide molecules between bulk and coordinated sites for mole fractions of water <0.75. The second was the indirect exchange of dimethyl sulphoxide molecules by replacement of dimethyl sulphoxide by water followed by replacement of water by dimethyl sulphoxide at mole fractions of water ≥ 0.8 (77). Other workers employed proton NMR to obtain equilibrium constants for the interaction of water with Al(III) ions in dimethyl sulphoxide (78).

A similar NMR study of Be(II) in dimethyl sulphoxide/water has been reported in the literature (79). Complexes resulting from the dissolution of Pd(II) in acetonitrile, dimethyl formamide or dimethyl sulphoxide (80) and of Zr(IV) in acetonitrile (81) have also been noted.

As mentioned above, numerous NMR studies on complex formation in metal salt-solvent or metal salt-mixed solvent have been performed. In many cases, however, perchlorate salts were used (62,65,66,78) but in other instances complexes of $M(CH_3CN)_6(ClO_4)_2$ (71,72,76) and $M(CH_3CN)_4(ClO_4)_2$ (73,62,79) (M = divalent metal) were synthesized and added to the solvent or mixed solvent. Metal-acetonitrile complexes without precise formula specifications were also prepared from various metal perchlorates with anhydrous acetonitrile, and were then added to the solvent (74). Only a few workers directly employed halide salts (70,75,77). The perchlorate salts or perchlorate complexes were used because they are stable species. Practical hydrometallurgical systems, however, contain acidic metal sulphates, metal sulphides or metal chlorides. Most of the potential applications of acetonitrile/water mixtures in copper hydrometallurgy deal with acidic solutions of copper sulphates (0.5-1 M) at ionic strengths of 0.1 to 2 M. To depict the formation of metal salt-solvent complexes in hydrometallurgical solutions, studies must be carried out using known quantities of acid (HCl or H_2SO_4), metal sulphate, sulphide, or chlorides that are added into the solvent or mixed solvent. Potentiometric methods normally employ salt concentrations of $\sim$0.01 M, and the results obtained may not directly reflect the behaviour of the complex in commercial hydrometallurgical systems. NMR, which is a less sensitive technique, may employ higher reagent concentrations. The effect of acid on the formation of metal salt-acetonitrile complexes has not yet been ascertained. Furthermore, proton, C-13, Al-27 and Sn-119 NMR studies have positively identified 1:1:1 ternary complexes of metal chlorides-Lewis base-HCl (82,83). The Lewis bases used were dimethyl ether and acetone; the metal chlorides used were $AlCl_3$, $SnCl_4$ and $TiCl_4$. A ternary 1:2:1 complex of

$SnCl_4$-acetophenone-HCl was also observed (82). It would be interesting to investigate whether organic nitrile, dimethyl formamide and dimethyl sulphoxide, which are also Lewis bases, behave in a similar way in the presence of metal chlorides and HCl.

ANALYTICAL REQUIREMENTS FOR THE DETERMINATION OF CATION OR ANION SPECIES IN MIXED SOLVENTS

Parker et al. measured Cu(I) and Cu(II) in mixed solvents by titrations against standard permanganate solution and thiosulphate solution, respectively. Iron interfered with both determinations (30). In the former case, air must be excluded during titration to avoid oxidation of Cu(I) to Cu(II). Iron does not interfere with the determination of copper by colourimetry with neocuproine (2,9-dimethyl-1, 10-phenanthroline) (84). Although this reagent reacts readily with copper(I), copper(II) also gives positive results (84). A better analytical method is required to determine Cu(I) and Cu(II) in the presence of iron(II) and iron(III).

In Parker's suggested process for the recovery of silver from crude silver chloride, the crude material was dissolved in dimethyl sulphoxide containing excess $CaCl_2$. Two equilibria occur; namely, $AgCl \rightleftarrows Ag^+ + Cl^-$ and $AgCl + Cl^- \rightleftarrows AgCl_2^-$ (40). Analysis of the solution by atomic absorption spectrometry does not speciate Ag^+ ion from $AgCl^-$ ion. An analytical method is required to measure $AgCl_2^-$ to understand better the dissolution kinetics of AgCl in dimethyl sulphoxide.

Several hydrometallurgical processes such as the leaching of scrap copper or chalcopyrite with $CuCl_2$ and/or $FeCl_3$ result in solutions of CuCl, $CuCl_2^-$ and $CuCl_3^{2-}$ together with various metal chloride impurities. Parker et al. suggested a recovery method for CuCl by extraction with acetonitrile and salting-out the acetonitrile-rich layer (37). An indirect

analytical method, with the addition of HCl or NaCl, led to the conclusion that CuCl was extracted more readily into the acetonitrile layer than was $CuCl_2^-$ (37). Fleming and Monhemius, however, found that aqueous acetonitrile solvents promoted the formation of $CuCl_3^-$, $CoCl_4^{2-}$ and $NiCl_4^{2-}$ during the ion exchange process (44). Based on the free energy of transfer of $AgCl_2^-$ ion (ΔG_{tr}) from water to acetonitrile (10 kJ/mol) and from water to dimethyl sulphoxide (7.5 kJ/mol) (40), these ions should be solvated in either solvent. It seems desirable to identify and measure directly such metal polychloride anions although no such method has yet been documented in the literature.

POSSIBLE EXPERIMENTAL PROGRAMS RELATED TO THE METALLURGICAL USE OF MIXED SOLVENTS

The above discussion has indicated several potential applications of mixed solvent systems in hydrometallurgical processing. Although much useful work has already been carried out in this area, many aspects of the problem remain to be resolved. The following discussion is intented to outline some general studies which could be carried out at CANMET to improve the understanding of mixed solvent systems, with particular emphasis on their use for copper processing or copper refining.

EXTRACTION OF COPPER

Extractants

Reagents which extract copper(I) but not copper(II) are the organic nitriles. Extractants such as dimethyl sulphoxide, dimethyl formamide, ketones, ethers, alkyl phosphites, alkyl phosphates, quarternary amines,

pyridines and diphenyl-thiocarbazone extract both copper(I) and copper(II). The extraction of copper with nitriles has been reported in detail (37). Based on the values of the free energy of transfer of ions from water to organic solvents, the following observations have been made (12,13). Dimethyl sulphoxide solvates Ag^+ to the same degree as it solvates Cu^+. It more readily solvates Cd^{2+}, Cu^{2+} and Zn^{2+} (no data are available for iron). Dimethyl formamide also solvates these metal ion impurities. These two extractants, therefore are not useful for purifying copper(I) from leaching solutions in acetonitrile/water. Ethers are not chosen because of the difficulty in handling them on an industrial scale. Diphenylthiocarbozone is not stable during storage. It must be purified before use and, therefore, is not practical (85). The distribution coefficient of copper(I) with tributyl phosphate (TBP) is greater than with the nitriles (37). The extraction with TBP has not been studied, however, because of the precipitation of CuCl between the TBP (neat) and the aqueous layer (37). This difficulty may be overcome by using a proper diluent and by selecting different alkyl phosphates. The extraction of copper(I) from aqueous chloride solutions with trialkyl phosphite has been patented (36). No attempt has been made, however, to use this extractant to recover copper(I) from aqueous acetonitrile solutions. Quarternary amine extracts metal ion-pairs ($CuCl_2^-$, $CuCl_3^{2-}$, etc.) and it is unlikely that copper(I) chloride will precipitate during extraction. The applications of ketones and pyridines for the extraction of copper(I) from acetonitrile/water solutions have not been reported. Based on the above data, the use of alkyl phosphite, alkyl phosphate and quarternary amines extractants should be examined in some detail to ascertain their utility in mixed solvent systems of relevance to metallurgical processing.

Diluent

The nature of the dilutent has a great influence on the rates of extraction/stripping, the metal ratios (e.g., Cu/Fe and Cu/Ag ratios) and the rate at which the aqueous and diluent phases separate after extraction. Also, acetonitrile will dissolve to a different extent in the various diluents. Therefore, aliphatic and aromatic diluents should be examined and the extraction results should be compared.

Effect of Acid and Neutral Salt Concentrations

The effect of an increase in the concentration of Na or Ca sulphates or chlorides at a fixed acid (H_2SO_4 or HCl) concentration on the distribution of Cu(I), Cu(II) and Cl^- in the aqueous and organic phases should be studied. The effect of an increase in acid concentration at a fixed salt concentration should also be examined. In these studies, two alternative methods of preparing the copper(I) solution should be tried. Firstly, known quantities of copper(II) and pure copper metal are placed in acetonitrile/water solution. The resulting copper(I) and the remaining copper(II) concentrations are then determined (by ion chromatography or titration) before the extraction is performed. Secondly, copper(I) chloride can be synthesized and a known quantity placed in the acetonitrile/water mixture. A synthesis method for copper(I) chloride is available (86).

Equilibrium Isotherm

The percentage extraction of Cu(I), Cu(II), Fe(II), Fe(III), Ag(I) and various metal ion impurities should be examined as a function of pH to obtain a characteristic $pH_{\frac{1}{2}}$ for each metal ion. The purpose is to find the ideal pH condition at which much of the Cu(I) and little of the other metal ions are extracted.

Distribution Coefficient

Comparisons should be made of the distribution coefficients of Cu(I), Cu(II), Fe(II), Fe(III), Zn(II), Co(II), Ni(II), Ag(I), Sb(III), Sb(V), As(III), As(V), Pb(II), etc. at particular concentrations of acid, neutral salt and metal chloride. The purpose of separating copper(I) from metal ion impurities suggests the importance of this study.

Extraction of Copper and Iron into the Organic Phase

Because iron(II) and iron(III) are the major impurities in the leaching solution, it is desirable to study the extraction of Cu(I), Cu(II), Fe(II) and Fe(III) from aqueous acetonitrile solutions containing all of these metal ions. The equilibrium $Cu(II) + Fe(II) \rightleftarrows Cu(I) + Fe(III)$ in the aqueous acetonitrile phase will be affected as the extraction of those species into the organic phase take place. It would be ideal if the distribution coefficients for Fe(III) and Cu(I) were higher than those for Fe(II) and Cu(II). If the distribution coefficient for Fe(III) is higher than that for Cu(I), after the stripping of the metal ions back into the aqueous acetonitrile (or just aqueous) system, significant amounts of Cu(II) and Fe(II) will be produced by the above equilibrium. Tbis will lead to a decreased recovery of Cu(I). Therefore, the interdependent effect of the concentration of these species, particularly at the start of the extraction, on the recovery of Cu(I) should be determined.

Rate of Extraction

A given reagent may extract a given metal ion faster than another metal ion. Thus, a knowledge of the rates of extraction of copper(I) and other metal ions is required to realize a good separation of copper(I) from various metal ion impurities.

Stripping

Copper(I) chloride precipitates in water, and copper(I) sulfate is unstable in water. Therefore, stripping with acidic water alone is not an ideal means of recovering copper(I) from the organic phase. An acetonitrile/water mixture is expected to stabilize either copper(I) chloride or copper(I) sulphate and, hence, may be used for stripping. The ratio of acetonitrile/water, as well as the acid concentration, should be determined to obtain a better recovery of copper(I) and a faster stripping rate, consistent with the lowest possible acetonitrile concentration in the aqueous phase.

Leaching Solutions

When all the above parameters have been investigated, studies must be made to extract copper(I) from process leaching solutions. For such a study, a good knowledge of leaching with acetonitrile/water is required. The leaching should take into account the suppression of impurities, in particular iron (30). As regards the potential application of the technique to copper refining, it would be desirable to perform research on the leaching of blister copper in acetonitrile/water.

COMPLEXES OF METAL SALTS WITH SOLVENTS

Emphasis should be placed on Cu(I) chloride because it has not been examined in previous NMR studies. Other metal chlorides of interest are those found as impurities in the copper leaching solution. The solvents should be acetonitrile, dimethyl sulphoxide and dimethyl formamide.

Chemical Shift of the Solvent

The CH_3-proton chemical shift of the solvent will be shifted to a lower field as its mole fraction in water increases while the water proton resonance is displaced to a higher field. In the presence of acid, the water molecule is protonated. Acid also protonates particular atoms in the solvent molecule (N in acetonitrile and dimethyl formamide, O in dimethyl sulphoxide). The electron shielding of the CH_3-group next to the protonated atom will be affected. Studies of the above two cases are important to understand the behaviour of the chemical shift of the solvent when metal salts are added to the solvent-water or solvent-water-acid systems.

NMR Study of Metal Salts in Pure Solvents

When a metal salt is dissolved in bulk solvent, a metal salt-solvent complex may be formed. The exchange of the CH_3-protons of the complex and those of the bulk solvent can be detected by NMR under favourable conditions. When the exchange rate is relatively slow, the CH_3-protons resonance due to the complex and to the bulk solvent appear separately. In this case, the chemical shift of the CH_3-protons of the complex directly characterizes the complex itself. When the exchange rate is faster, the CH_3-protons resonance of the complex and the bulk solvent coalesce together as a relatively broad peak. In this case, the chemical shift of the coalescence peak is a function of the concentration of the complex. By varying the initial concentration of the metal salt and measuring the chemical shift of the coalescence peak, the chemical shift of the complex is determined. Evaluation of the integration data of the resonance peaks from a series of experiments during which the metal salt concentrations are varied provides the coordination number of the solvent to the metal salt and the equilibrium

constant for the formation of the complex. The Arrhenius activation energy can be obtained from the experimental data at various temperatures. This relationship also provides other thermodynamic parameters such as the enthalpy (ΔH) and entropy (ΔS) of the exchange process. Often, it is shown that the formation of more than one complex occurs. Similar experiments in the presence of known quantities of acid would provide information on the possible formation of metal salt-solvent-acid complexes.

NMR Study of Metal Salts in Mixed Solvent-Water Media

Experiments should be performed by varying the mole fraction of the solvents at various fixed concentrations of the metal salt. From the dependence of the CH_3-protons chemical shifts on the mole fraction of the solvent, the coordination number of the solvent to the metal ion can be deduced. From the shift of the water resonance, the change in the hydration of the metal ion may be followed. Such experiments, therefore, would allow the observation of the change from hydration of the metal ion to selective solvation. The effect of the presence of acid and the possible formation of metal salt-solvent-hydrate-acid complex(es) could also be investigated.

C(13) and N(14) NMR Studies

A C(13) NMR study would supplement the proton NMR data, and would provide further details of the structure of the complexes. Multiplicity-determining carbon resonance spectra have been useful in the description of the $SnCl_4$-ketone-HCl complexes and $TiCl_4$-ether-HCl complexes (82,83). Because acetonitrile and dimethyl formamide have N atoms in their molecules, N(14) NMR could also be useful.

ANALYSIS OF CATION OR ANION SPECIES IN MIXED SOLVENTS

Determination of Fe(II), Fe(III), Cu(I) and Cu(II)

Dionex cation chromatography with column HPIC-CS5 can separate Cu(II), Fe(II) and Fe(III) (89). The eluant is 6 mM pyridien-2, 6-dicarboxylic acid whose pH has been adjusted to 4.8 with LiOH. The effluent can be reacted with 0.4 mM 2,4-pyridyl azoresorcinol reagent and the three peaks due to these cations are detected with a UV-Visible detector at 520 nm. A typical separation done by Dionex gave retention times of 5, 8 and 16 min for Fe(III), Cu(II) and Fe(II), respectively. It seems possible to devise an analytical method for the determination of these cations in acetonitrile-water solutions. Because the volume of the sample injected into the ion chromatograph is 0.5 µL, the acetonitrile entering into the column is probably too little to damage the column. Normally, a HPIC ion chromatography column can tolerate up to 25% acetonitrile solution (90). Acetonitrile itself is not detected at the wavelength of the measurement.

The separation example from Dionex does not incorporate Cu(I) ion. An attempt should be made to detect and measure the Cu(I) ion. It would likely be necessary to prepare the primary CuCl standard in degassed acetonitrile and then dilute it to lower concentration standards in degassed acetonitrile-water. The concentration of Cu(I) may also be obtained by difference of the total copper and Cu(II). Total copper can be measured as Cu(II) after sample oxidation with aqua regia.

For the analysis of concentrated samples, the ion chromatography method would have to be verified for the possible change in the concentration ratios of the species during dilution before injection. Any such change could be minimized by dilution using a mixed solvent with the same proportion of acetonitrile and water.

Determination of Metal Chloride Anions

In the recovery of silver from AgCl mentioned earlier, determination of AgCl and $AgCl_2^-$ species in dimethyl sulphoxide solution is required. The $AgCl_2^-$ ion is solvated in dimethyl sulphoxide and in acetonitrile (46). It is known that $Au(CN)_2^-$, $Au(CN)_4^-$, $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ can be separated by a MPIC ion chromatography column with a liquid mobile phase of acetonitrile-water (91). Similarly, the $AgCl_2^-$ ion may also be detectable by mobile phase ion chromatography with conductivity detection. To stabilize this anion during its passage through all the ion chromatography routes, a liquid mobile phase consisting of either acetonitrile-water or dimethyl sulphoxide-water will be used. Tributyl ammonium hydroxide (a base which is soluble in solvent) will be added to the liquid mobile phase to make it basic and therefore enhance the elution of the analyte anions. The ideal ratio of acetonitrile-water or dimethyl sulphoxide-water in the liquid mobile phase will be investigated. An extension of this study to other metal chloride anions, such as $FeCl_4^-$, $CuCl_2^-$, etc., seems possible because these anions are also well solvated in acetonitrile (37).

Since this type of metal chloride ion has not been detected previously by ion chromatography, the preliminary step would be to prove its detectability. Therefore, a series of solutions with a fixed concentration of AgCl and variable amounts of chloride (e.g., NaCl or $CaCl_2$) would be prepared and injected into the ion chromatograph. The peak height of the $AgCl_2^-$ ion, which is proportional to its conductivity, would be measured. The relationship of conductivity to Cl^- ion concentration should reflect the cumulative formation constant for $AgCl_2^-$ according to the equation $AgCl + Cl^- \rightleftarrows AgCl_2^-$. The value obtained could also be compared to that from the potentiometric method. The following step would be to define

the peak height (or conductivity) at which the concentration of $AgCl_2^-$ may be assumed as a standard (standard compounds for metal chloride anions are not available). Hopefully, the information obtained could then be used for the analysis of anions in the unknown samples.

CONCLUSIONS

1 - Several potential applications of mixed aqueous-organic systems to hydrometallurgical processing have been identified. Although a number of systems have been studied, most emphasis has been placed on the leaching of copper-bearing feeds by acetonitrile-$CuSO_4$-H_2SO_4 media. Such solutions can yield, on distillation of the acetonitrile, a copper powder product comparable in purity to commercial cathode copper. The use of mixed solvent systems, therefore, holds some promise for copper refining although much work would have to be done to implement such a process. The use of mixed solvent systems for refining crude AgCl also seems promising, but would also require extensive development.

2 - A number of studies on the chemical aspects of mixed solvent systems have been carried out. These investigations have emphasized activity changes occurring when an ion is transferred from the aqueous to the organic phase and have also stressed the different solvation properties of ions in the two phases.

3 - Many of the fundamental aspects of mixed solvent systems are yet to be resolved. Some of the areas requiring further study include the use of different extractants and diluents as well as variations in the leaching system and leaching conditions. The use of NMR to elucidate the solvation of metal ions and ion chromatography to clarify some aspects of complex formation is strongly recommended.

ACKNOWLEDGEMENTS

The author acknowledges the assistance of J.E. Dutrizac and J.B. O'Reilly with the preparation of this report.

REFERENCES

1 - Parker, A.J. "The effects of solvation on the properties of anions in dipolar aprotic solvents"; Quart Rev (London) 16:163-187; 1962.

2 - Parker, A.J. "Rates of bimolecular substitution reactions in protic and dipolar aprotic solvents"; Adv Phys Org Chem 5:173-235; 1967.

3 - Parker, A.J. "Protic-dipolar aprotic solvent effects on rates of bimolecular reactions"; Chem Rev 69:1:1-32; 1969.

4 - Cox, B.G., Natarajan, R. and Waghorne, W.E. "Thermodynamic properties of transfer of electrolytes from water to acetonitrile and to acetonitrile + water mixtures"; J Chem Soc Faraday Trans I 86-95; 1979.

5 - Das, K., Das, A.K. and Kundu, K.K. "Ion-solvent interactions in acetonitrile + water mixtures"; Electrochimica Acta 26:471-478; 1981.

6 - Wells, C.F. "Ionic solvation in water + Co-solvent mixtures"; J Chem Soc Faraday Trans I 77:1515-1528; 1981.

7 - Kundu, K.K. and Parker, A.J. "Solvation of Ions. XXVII. Comparison of methods to calculate single ion free energies of transfer in mixed solvents"; J Solution Chem 10:847-861; 1981.

8 - Boyd, R.H. "Acidity functions" in Solute-Solvent Interactions; edited by Coetzee, J.F. and Ritchie, C.D.; Dekker; New York, NY; 1969.

9 - Parker, A.J. "Ionic equilibrium in protic and in dipolar aprotic solvents"; Pure and Appl Chem 25:345-363; 1971.

10 - Parker, A.J. "Solvation of ions - Some applications"; Proc Roy Aust Chem Inst 39:163-170; 1972.

11 - Parker, A.J. "Hydrometallurgy of copper and silver in solvent mixtures"; Search 4:426-432; 1973.

12 - Parker, A.J. "Solvation of ions. Applications to minerals and energy"; Pure and Appl Chem 53:1437-1445; 1981.

13 - Muir, D.M. and Parker, A.J. "Applications of non-aqueous and mixed aqueous-organic solvents to chloride hydrometallurgy"; Hydrometall Res Dev Plant Pract, Proc Int Symp, 3rd; edited by Osseo-Asare, K. and Miller, J.D.; TMS-AIME; Warrendale, Pennsylvania; 341-355; 1983 (Pub. 1982).

14 - Parker, A.J., Muir, D.M., Sharp, J.H., Waghorne, W.E., Alexander, R. and Giles, D.E. "An excellent method of recovering high purity particulate of copper"; British Patent 1 381 666; 1975.

15 - Parker, A.J., Waghorne, W.E., Sharp, J.H. and Muir, D.M. "Electrorefining of copper in copper(I) sulfate solutions"; Ger Offen 2 218 269; 1972.

16 - Parker, A.J., Wagnorne, W.E., Giles, D.E., Sharp, J.H., Alexander, R. and Muir, D.M. "Use of copper salts in the reocvery of copper from copper-containing materials"; Ger Offen 2 216 383; 1972.

17 - Parker, A.J.; Belgian Patent 781 608; 1972.

18 - Parker, A.J. and Muir, D.M. "Copper from copper concentrates via solutions of cuprous sulfate in acetonitrile-water solutions"; Extr Metall Copper Int Symp; TMS-AIME, Warrendale; 2:963-973; 1976.

19 - Muir, D.M., Parker, A.J. and Giles, D.E. "Cuprous hydrometallurgy. Part V. Leaching of copper-lead matte with copper(II) sulphate in aqueous acetonitrile"; Proc Australas Inst Min Metall 272:5-12; 1979.

20 - Parker, A.J. and Muir, D.M. "Recovery of copper powder from copper concentrates and from solutions of copper(II) sulfates using sulfur dioxide and aqueous acetonitrile"; Hydrometallurgy 6:239-260; 1981.

21 - Parker, A.J.; Australian Patent 40296; 1972.

22 - Parker, A.J.; Australian Patent 40298; 1972.

23 - Parker, A.J., Muir, D.M., Giles, D.E., Alexander, R., O'Kane, J. and Avraamides, J. "The leaching of copper from sulphur activated chalcopyrite with cupric sulfate in nitrile-water mixtures"; Hydrometallurgy 1:169-181; 1975.

24 - Muir, D.M., Parker, A.J. and Giles, D.E. "Cuprous hydrometallurgy. Part IV. Rates and equilbira in the reaction of copper sulphides with copper(II) sulphate in aqueous acetonitrile"; Hydrometallurgy 2: 127-140; 1976.

25 - Avraamides, J., Muir, D.M. and Parker, A.J. "Cuprous hydrometallurgy. Part VI. Activation of chalcopyrite by reduction with copper and solutions of copper(I) salts"; Hydrometallurgy 5:325-336; 1980.

26 - Muir, D.M., Parker, A.J., Sharp, J.H. and Waghorne, W.E. "Cuprous hydrometallurgy. Part I. Electrorefining copper via acidic solutions of cuprous sulphate containing organic nitriles"; Hydrometallurgy 1: 61-77; 1975.

27 - Muir, D.M., Parker, A.J., Sharp, J.H. and Waghorne, W.E. "Cuprous hydrometallurgy. Part II. The electrowinning of copper from cuprous sulphate solutions containing organic nitriles"; Hydrometallurgy 1: 155-168; 1975.

28 - Cathro, K.J. "Segregation and acetonitrile leaching tests on Ukaparinga copper ore"; Proc Australas Inst Min Metall 248:17-21; 1973.

29 - Lu, Z.Y., Grimsey, E.J. and Parker, A.J. "Copper separation from iron and nickel-iron-sulfide concentrates by a double-roast, acetonitrile leaching process"; Proc Australas Inst Min Metall 288:19-27; 1983.

30 - Parker, A.J., Muir, D.M., Smart, Y.C. and Avraamides, J. "An application of acetonitrile leaching and disproportionation. Refining segregated copper from roasted concentrates and ores"; Hydrometallurgy 7:213-233; 1981.

31 - Parker, A.J. and Muir, D.M. "Recovery of copper from materials containing copper and acid soluble iron compounds"; Australian Patent 504 426; 1979.

32 - Muir, D.M., Benari, M.D., Clare, B.W., Mangano, P. and Parker, A.J. "Removal of iron(II) and copper(II) by addition of chloride ion or acetonitrile"; Hydrometallurgy 9:257-275; 1983.

33 - Milner, E.F.G., Peters, E., Swinkels, G.M. and Vizsolyi, A.I. "Copper hydrometallurgy"; U.S. Patent 3 798 026; 1979.

34 - Swinkels, G.M. "Extraction of copper chlorides from aqueous solutions"; Ger Offen 2 635 855; 1973.

35 - Demarthe, J.M., Gandon, L. and Georgeaux, A. "A new hydrometallurgical process for copper"; Extractive Metallurgy of Copper, Vol. II, Hydrometallurgy and Electrowinning; edited by Yannopoulos, J.C. and Agarwal, J.C.; TMS-AIME, 825-848:1976.

36 - Healy, T.V. and Pilbeam, A. "Solvent extraction and electrowinning of copper"; U.S. Patent 3 703 451; 1975.

37 - Preston, J.S., Muir, D.M. and Parker, A.J. "Cuprous hydrometallurgy. Part VIII. Solvent extraction and recovery of copper(I) chloride with organic nitriles from an iron(III), copper(II) chloride, two-step oxidative leach of chalcopyrite concentrate"; Hydrometallurgy 5: 227-241; 1980.

38 - Parker, A.J., Muir, D.M., Grimsey, E.J. and Preston, S. "Copper(I) chloride from ores with acetonitrile"; U.S. Patent 4 308 289; 1981.

39 - Grimsey, E.J., Muir, D.M. and Parker, A.J. "Cuprous hydrometallurgy. Part VII. Separation and purification of copper(I) chloride from a chlorination roast of Kambalda nickel matte using solutions of aqueous acetonitrile"; Proc Australas Inst Min Metall 273:210-251; 1980.

40 - Parker, A.J., Claire, B.W. and Smith, R.P. "Solvation of ions. Some applications IV. A novel process for the recovery of pure silver from impure silver chloride"; Hydrometallurgy 4:233-245; 1979.

41 - Korkisch, J. and Ahluwalia, S.S. "Cation-exchange behavior of several elements in hydrochloric acid-organic solvent media"; Talanta 14: 150-170; 1967.

42 - Strelow, R.W.E. "Application of ion exchange to element separation and analysis" in Ion Exchange and Solvent Extraction, Vol. 5; edited by Marinsky, J.A. and Marcus, Y.; Dekker; New York; NY; 1973.

43 - Marcus, Y. "Ion exchange in non-aqueous and mixed solvents"; in Ion Exchange and Solvent Extraction, Vol. 4; edited by Marinsky, J.A. and Marcus, Y.; Dekker; New York, NY; 1973.

44 - Fleming, C.A. and Monhemius, A.J. "On the extraction of various base metal chlorides from polar organic solvents into cation and anion exchange resins"; Hydrometallurgy 4:159-167; 1979.

45 - Parker, A.J., Waghorne, W.E., Giles, D.E., Sharp, J.H., Alexander, R. and Muir, D.M.; U.S. Patent 3 865 744; 1975.

46 - Parker, A.J. "Recovery of metal values"; PCT Int Appl WO 82 00 478; 1980.

47 - Parker, A.J. and Muir, D.M.; Canadian Patent 390 706; 1981.

48 - Parker, A.J. "Nitrile solutions to energy problems"; Studies in Physical and Theoretical Chemistry 27:313-324; 1982.

49 - Muir, D.M. "Recovery of gold from cyanide solutions using activated carbon: A review"; Symp Ser, Australas Inst Min Metall (Carbon Pulp Technol. Extr. Gold) 32:7-22; 1982.

50 - Parker, A.J. and Muir, D.M. "Stripping gold or silver from particulate materials"; South African Patent ZA 81 07 908; 1982.

51 - Parker, A.J. and Muir, D.M. "Composition for stripping gold or silver from particulate materials"; U.S. Patent 4 427 571; 1984.

52 - Libus, W., Pilarczyic, M., Strzelecki, H. and Gryzybkowski, W. "Leaching copper-bearing sulphidic materials with pyridine-chloroform mixtures"; Hydrometallurgy 10:397-403; 1983.

53 - Libus, W., Pilarczyk, M., Strzelecki, H. and Grzybkowski, W.; U.S. Patent 4 269 676; 1983.

54 - Pilarczyk, M., Strzelecki, H. and Grzybkowski, W. "Recovery of copper from chalcocite by means of the pyridine and chloride ion donor systems"; Hydrometallurgy 11:247-251; 1983.

55 - Harrison, W.D., Gill, J.B. and Goodall, D.C. "Reactions in mixed non-aqueous systems containing sulfur dioxide. Part I"; J Chem Soc Dalton Trans 1431-1433; 1978.

56 - Harrison, W.D., Gill, J.B. and Goodall, D.C. "Reactions in mixed non-aqueous systems containing sulfur dioxide. Part II"; J Chem Soc Dalton Trans 847-850; 1979.

57 - Gill, J.B., Goodall, D.C. and Harrison, W.D. "The solution of metals in dimethyl sulphoxide and other non-aqueous solvents containing sulphur dioxide"; Hydrometallurgy 6:347-351; 1981.

58 - Strehlow, H. "Chemistry of non-aqueous solvents", Vol. I; edited by Lagowski, J.J.; Academic Press; New York; 1966.

59 - Clare, B.W., Mangano, D.M., Muir, D.M., Parker, A.J. and Singh, P. "Hydrometallurgical thermodynamics I. Effect of sulfate ion pairing and ion solvation on the copper-iron redox equilibrium in aqueous acetonitrile"; Aust J Chem 36:1687-1694; 1983.

60 - Pawelka, F. "Organic Ag complexes"; Z Electrochem 30:180-184; 1924.

61 - Koch, F.K. "A simple electrochemical method for the simultaneous determination of the constitution and equilibrium constant of complex ions in solution. Application to complex silver ions"; J Chem Soc 2053-2063; 1930.

62 - Manahan, S.E. and Iwamoto, R.T. "Complexes of copper(I) and silver(I) with acetonitrile in water, the lower alcohols, acetone and nitroethane"; J Electroanal Chem 14:213-217; 1967.

63 - Singh, P., MacLeod, I.D. and Parker, A.J. "Solvation of ions, Part XXX. Thermodynamics of transfer of copper ions from water to solvent mixtures"; J Solution Chem 11:495-508; 1982.

64 - Singh, P., MacLeod, I.D. and Parker, A.J. "Solvation of ions. Part XXIX. Ionic conductances in acetonitrile-water and pyridine-water mixtures"; J Solution Chem 13:103-119; 1984.

65 - Schneider, H. "Ion solvation studied by NMR and electrochemical methods"; Electrochimica Acta 21:711-718; 1976.

66 - Clausen, A., El-Harakany, A.A. and Schneider, A. "Studies of silver(I) solvation in binary solvent mixtures containing dimethyl sulphoxide II. NMR investigations of the shift in the preferential solvation of silver ions from water to DMSO"; Ber Bunsenges Phys Ch[illegible] 77:994-997; 1973.

67 - MacLeod, I.D., Parker, A.J. and Singh, P. "Electrochemistry of copper in aqueous acetonitrile"; J Solution Chem 10:757-774; 1981.

68 - Jayasekera, S., Avraamides, J. and Parker, A.J. "Solvation of ions. Some applications V. Electrolytic recovery of silver from non-aqueous solutions"; Aust J Chem 36:1695-1704; 1983.

69 - Parker, A.J., Douglas, A.C., Couche, R.A., Miller, G., Tilley, R.I. and Waghorne, W.E. "Solvation of ions. Some applications III. Solutions of copper(I) salts in water containing ligands"; Aust J Chem 30:1661-1672; 1977.

70 - Horvath, V.E., Sykora, J. and Gazo, J. "Thermal and photochemical properties of chloro copper(II) complexes in acetonitrile. I."; Z Anorg Allg Chem 442:235-244; 1978.

71 - Kapur, V.K. and Wayland, B.B. "Nitrogen-14 contact shifts and line broadening studies for acetonitrile complexes of copper(II), nickel(II), cobalt(II) and titanium(III)"; J Phys Chem 77:634-637; 1973.

72 - West, R.J. and Lincoln, S.F. "The exchange of acetonitrile on iron(II) in acetonitrile solvent. A nitrogen-14 nuclear magnetic resonance study"; Aust J Chem 24:1169-1175; 1971.

73 - West, R.J. and Lincoln, S.F. "Nitrogen-14 magnetic resonance study of the exchange of acetonitrile on copper(II) complexes"; J Chem Soc Dalton Trans I 281-284; 1974.

74 - Vigee, G.S., Watkins, C.L. and Harris, M.E. "NMR line broadening studies of transition metal complexes in acetonitrile solution"; J Inorg Nucl Chem 42:1441-1445; 1980.

75 - Banewicz, J.J., Maguire, J.A., Smith, P.O., Lussky, D., Sudbrink, D.W. and Allen, D.E. "A thermodynamic investigation of cobalt(II) bromide + acetonitrile and cobalt(II) bromide + propionitrile"; J Chem Thermodynamics 13:629-633; 1981.

76 - Frankel, L.S., Stengle, T.R. and Langford, C.H. "Preferential solvation of Co^{2+} and Ni^{2+} ions in mixed solvents: NMR methods"; Can J Chem 46:3183-3187; 1968.

77 - Thomas, S. and Reynolds, W.L. "Proton magnetic resonance study of aluminum(III) chloride in water-dimethyl sulfoxide solvent mixtures"; Inorg Chem 9:78-81; 1970.

78 - Olander, D.P., Marianelli, R.S. and Larson, R.C. "Solvation of aluminum(III) ion in dimethylsulfoxide-water solutions by proton magnetic resonance spectrometry"; Anal Chem 41:1097-1099; 1969.

79 - Fuldner, H.H., Devia, D.H. and Strehlow, H. "Substitution reactions of beryllium(II) ion in mixed solvents. II. Solvent exchange between the inner solvation shell and the bulk in dimethyl sulphoxide and dimethyl sulphoxide/water mixtures"; Ber Bunsenges Phys Chem 82: 499-503; 1978.

80 - Volchenskova, I.I. and Yatsimirskii, K.B. "Charge transfer bands and conformation of palladium chloride solvates in some donor solvents"; Teor Eksp Khim 13:197-204; 1977; Chem Abstr 87:31367a.

81 - Kharitonov, Yu.Ya., Nikitin, K.N. and Gasanov, T.A. "Formation of acetonitrile complexes of zirconium in the anodic dissolution of zirconium"; Zh Neorg Khim 25:971-974; 1980; Chem Abstr 92:204359h.

82 - Tan, L.K. and Brownstein, S. "Equilibria and reactions in the systems aluminum chloride-acetyl chloride-aromatic hydrocarbon in sulfur dioxide as solvent"; J Org Chem 48:302-306; 1983.

83 - Tan, L.K. and Brownstein, S. "Complexes of $TiCl_4$ of interest in Friedel-Crafts reactions"; Inorg Chem 23:1353-1355; 1984.

84 - Smith, F.G. and McCurdy, W.H. "2,9-dimethyl-1, 10-phenanthroline, new specific in spectrophotometric determination of copper"; Anal Chem 24:371-373; 1952.

85 - Geiger, R.W. and Sandell, E.B. "Cu(II)-dithizone equilibrium in water-CCl_4"; Anal Chim Acta 8:197-208; 1953.

86 - Jindra, J. and Perner, B. "Preparation of high purity CuCl"; Chem Prumysl 15:9:560-561; 1965; Chem Abstr 63:15819f.

87 - Kirgintsev, A.N. and Raspopin, S.I. "Synthesis and purification of copper(I) chloride and production of its single crystals in a rotating container"; Deposited Publ VINITI; 4167-4172; 1972; Chem Abstr 85:40211f.

88 - O'Donnell, J.F., Ayres, J.T. and Mann, C.K. "Preparation of high purity acetonitrile"; Anal Chem 9:1161-1162; 1965.

89 - Dionex News Note 11/15/84.

90 - Dionex Technical Note 2R "Routine maintenance and reconditioning of columns"; 1983.

91 - Dionex Application Note "The determination of Au^{+} and Au^{3+} in gold cyanide plating bath"; 40R; October 1983.